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TEST OF EXPLOSIVE COMPOUNDS

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14. ABSTRACT

This report contains a summary of compounds submitted to Picatinny Arsenal, Dover, New Jersey by Arthur D. Little, Inc. for heat of combustion determination. When sufficient sample was available, stability and sensitivity tests were also made. Except for two compounds, namely Medina (methylene dinitramine) and bis(2,2,2-trinitroethyl)urea, all those tested whose performance was outstanding were unsatisfactory for use as military high explosives because of poor thermal stability, extreme sensitivity, or both.

15. SUBJECT TERMS

Medina (methylene dinitramine) Bis(2,2,2-trinitroethyl)urea Explosive compounds

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OBJECTIVES

The objective of these tests was to evaluate as explosives, compounds submitted to Picatinny Arsenal, Dover, New Jersey by Arthur D. Little, Inc. under Army contract W-19-020-ORD-6436.

SUMMARY

Several compounds were submitted to Picatinny Arsenal by Arthur d. Little, Inc. for heat of combustion determination. When sufficient sample was available, stability and sensitivity tests were also made. Except for two compounds, namely, Medina (methylenedinitramine) and bis(2,2,2-trinitroethyl)urea, all those tested whose performance was outstanding were unsatisfactory for use as military high explosives because of poor thermal stability, extreme sensitivity, or both.

Bis(2,2,2-trinitroethyl)urea and methylenedinitramine are unusual as explosives from two standpoints: (a) they are oxygen balanced to carbon dioxide and water and (b) they possess outstanding power. For these reasons, it is believed that further study for them is warranted, although the first mentioned is undesirably sensitive to impact, while the second does not appear sufficiently stable.

INTRODUCTION

Under Army contract W-19-020-ORD-6436, Arthur D. Little, Inc. has synthesized a number of explosive compounds. These were forwarded to Picatinny Arsenal for determination of heat of combustion values. When sample size permitted, the compound was further evaluated by tests standard at Picatinny Arsenal.

The following compounds were received here:

Nitroform™
Trinitroethanol
Trinitroacetonitrile
Bis(2,2,2-trinitroethyl)urea
Ethylenediamine salt of Nitroform™
Dinitrotrifluoromethylbenzene
Pentanitroaniline
2,3,4,6-tetranitromethylphenylnitramine
Trinitrotriazidobenzene
Hexamethylobenzenehexanitrate
Tetra-B-nitroxyethyl ammonium nitrate
Hexanitrosobenzene
1,1-dinitropropane
Picryl allyl ether
Picryl propargyl ether
Picryl popyl ether
N,N'-dichlorohaleite
Compound 335 (so-called tetranitrobutane)
Methylenedinitramine (Medina)
2,3,4,5-tetranitrophenylmethylnitramine (Submitted to Picatinny Arsenal as pentanitrophenylmethylnitramine)

Considerable test data were collected and it seemed desirable to compile the data obtained to date and to assess the potential military value of the compounds. This report presents such a compilation.

RESULTS

The determined heat of combustion value of each of the compounds examined is given in table 1. The heat of combustion of N,N'-dichlorohaleite was not determined because of its extreme instability and high sensitivity.

Table 1

	Empirical formula	Molecular weight	Oxygen balance CO	Oxygen balance CO_2	Heat of combustion (cal/gm)
Nitroform™	CHN_3O6	151	⁄48	⁄37	823
Trinitroethanol	$C_2H_3N_3O_7$	181	⁄31	⁄13	1291
Trinitroacetonitrile	$C_2N_4O_6$	176	⁄36	⁄18	1324
Bis(2,2,2-trinitroethyl)urea	$C_5H_6N_8O_{13}$	386	⁄21	0	1561
Methylenedinitramine	$CH_4N_4O_4$	136	⁄12	0	1626
Ethylenediamine salt of Nitroform™	$C_4H_{10}N_8O_{12}$	362	⁄13	-4.5	1830
Dinitrotrifluoro-methylbenzene	$C_7H_{10}N_8O_{12}$	236	-30	-75	2130
Pentanitroaniline	$C_6H_2N_6O_{10}$	318	⁄15	-15	2156
2,3,4,6-tetranitro-methylphenylnitramine	$C_7H_4N_6O_{10}$	332	⁄5	-29	2510
Trinitrotriazidobenzene	$C_6N_{12}O_6$	336	0	28.5	2554
Hexamethylolbenzene-hexanitrate	$C_{12}H_{12}N_6O_{18}$	528	0	-36	2653
Tetra-B-nitroxyethyl ammonium nitrate	$C_8H_{16}N_6O_{15}$	436	-4	-40	2678
Hexanitrosobenzene	$C_6N_6O_6$	252	0	-38	2707
1,1-dinitropropane	$C_3H_6N_2O_4$	134	-24	-60	3349
Picryl allyl ether	$C_9H_7N_3O_7$	269	-33	-86	3971
Picryl propargyl ether	$C_9H_5N_3O_7$	267	-27	-81	3974
Picryl popyl ether	$C_9H_9N_3O_7$	271	-38	-92	4075
N,N'-dichlorohaleite	$C_2H_4N_4O_4Cl_2$	219	0	-15	--
2,3,4,5-tetranitrophenyl-methylnitramine	$C_7H_4N_6O_{10}$	332	⁄5	-29	2453

Table 2 lists the results of thermal stability, impact sensitivity, brisance, and explosion temperature tests conducted on the subject compounds. For the purpose of comparison, there are included in this table the results of the same tests of the explosives TNT, RDX, PETN, lead azide, and mercury fulminate.

Table 2
Properties of explosive compounds

	Impact test			100°C heat test			90°C heat test			75°C heat test								
	BM app	PA app		% loss			% loss			% loss			90°C vac stab test			Sand test	Expl temp	Melt pt
	2 kg (cm)	2 kg (cm)	Chg wgt (mgs)	1st 48 hrs	2nd 48 hrs	Expl in 100 hrs	1st 48 hrs	2nd 48 hrs	Expl in 100 hrs	1st 48 hrs	2nd 48 hrs	Expl in 100 hrs	Wgt, gm	Hrs	cm^3	gm	°C	°C
Nitroform™	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	26.5
Trinitroethanol	-	-	-	68	26	None	-	-	-	-	-	-	-	-	-	-	-	-
Trinitroacetonitrile	≤15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Bis(2,2,2-trinitroethyl)urea	9	3	13	2.6	12.1	None	-	-	-	-	-	-	1	40	2.95	61.0	-	-
Methylemedinitramine	19	5	17	38	-	None	23.8	6.9	None	0.5	0.6	None	1	17	11/	63.1	-	104-105
N,N'-dichlorohaleite	-	4	16	Expl in 30 min			-	-	-	-	-	-	-	-	-	55.0	120	-
Ethylenediamine salt of nitroform	-	-	-	Burned in 1.5 hr			-	-	-	-	-	-	-	-	-	-	-	-
Dinitrotrifluoro-methylbenzene	-	>70	32	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pentanitroaniline	9-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	190-192[b]
2,3,4,6-tetranitrophenyl-methylnitramine	19	6	14	8.62	1.29	None	7.02	1.78	None	0.90	3.24	None	1	28	11/	-	-	146-147
2,3,4,5-tetranitrophenyl-methylnitramine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	130-0.05
Trinitrotriezidobenzene	≤25[c]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	150	-
Hexamethylolbenzene hexanitrate	-	≤3	20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	176-177
Tetra-B-nitroxyethyl ammonium nitrate	12	5	7	67	2	None	-	-	-	2.17	26.10	None	0.5[a]	16	11/	-	-	-
Hexanitrosobenzene	-	3	13[d]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1,1-dinitropropane	100/[e]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Picrylallylether	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	88-99
Picrylpropargyl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	100-101
Picrylpropylether	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	43.5-44.0
TNT	100/	14	17	0.2	0.2	None	-	-	-	-	-	-	5.0[f]	40	0.23	48.0	475	81-82
RDX	32	8	18	0.04	Nil	None	-	-	-	-	-	-	5.0[f]	40	0.9	60.2	260	204
PETN	17	6	16	0.1	None	None	-	-	-	-	-	-	5.0[a]	40	0.5	62.7	225	141
Lead axide-dextrinated	17	5	28	0.34	0.05	None	-	-	-	-	-	-	1.0[a]	40	1.0	19.0	340	-
Mercury fulminate	5[g]	2	30	Expl in 40 hrs			-	-	-	-	-	-	-	-	-	23.4	210	-

[a]100° vac stab test. [b]Copper block-uncorrected value. [c]500 gm weight. [d]4-5 in. with 20 mg charge. [e]Liquid method. [f]120°C vac stab test. [g]35 cm, 1 kg wgt.

Discussion of Results

For an explosive material to be even considered for possible military use, it must pass vigorous preliminary stability, sensitivity, and power tests. All test results must then be evaluated against standard military explosive materials now in use. This is true regardless of whether the material is envisioned for use as a high explosive per se or as a component in a propellant composition. The materials submitted were evaluated from this point of view.

Nitroform™, 1,1-dinitropane, dinitrotrifluoromethylbenzene, picryl allyl ether, picryl propargyl ether, and picryl propyl ether were subjected only to the heat of combustion determination. By virtue of their empirical composition, further study of the picryl ethers is not warranted. Likewise, on the basis of its poor stability properties, Nitroform™ does not merit additional study.

On the basis of stability and/or sensitivity characteristics, the following compounds are considered to be unsuitable for military use and therefore not worthy of further investigation. This evaluation is made from the data contained in table 2.

Compound	Stability	Sensitivity class
Trinitroethanol	Poor	-
Trinitroacetonitrile	Volatile	More sensitive than PETN
N,N'-dichlorohaleite	Very poor	Lead azide
Ethylenediamine salt of Nitroform™	Poor	-
Pentanitroaniline	Poor	Lead azide
2,3,4,6-tetranitromethylphenylnitramine	Poor	PETN
Trinitrotriazidobenzene	-	More sensitive than mercury fulminate
Hexamethylolbenzenehexanitrate	-	Mercury fulminate or worse
Tetra-B-nitroxylethyl ammonium nitrate	Poor	Lead azide
Hexanitrosobenzene	-	Mercury fulminate or worse

It should be recalled that mercury fulminate was eliminated and PETN virtually so from military use because of sensitivity and/or poor stability properties. They have been used only as reference standards to indicate the class of the material being evaluated. The classification of 2,3,4,6-tetranitromethylphenylnitramine (m-nitrotetryl) as being of poor stability is based on data given in Blatt, OSRD report 2014.

As noted earlier in this report, two compounds, namely, bis(2,2,2-trinitroethyl)urea and methylenedinitramine (Medina) are judged to warrant further study before being discarded. Both are powerful explosives, being oxygen balanced to carbon dioxide and water. The data in table 2 indicates bis(2,2,2-trinitroethyl)urea to be of fair stability, but of high sensitivity. The compound is made from dimethylol urea, which is difficult to isolate in the pure monomeric state, and it is probable that impurities are present. It seems desirable to determine if this is so, and to prepare and study the pure compound, if possible. The second compound, Medina, if capable of further stabilization, could find use as an additive to less sensitive and poorly oxygen balanced castable explosives. It is believed that each of these compounds should be re-examined very thoroughly, using only materials of the highest purity obtainable.

In addition to this, a compound alleged to be 2,2,3,3-tetranitrobutane was submitted for testing. Theoretically, this compound, a solid, white crystalline material melting over 100°C, has an oxygen balance to carbon dioxide and water of -20. The material submitted was indicated to be of reasonably good thermal stability and rather high impact sensitivity. However, repeated elemental analyses does not allow a structure of 2,2,3,3-tetranitrobutane to be assigned to the material submitted. Work is in progress to purify this material and determine its true structure.

EXPERIMENTAL PROCEDURE

All tests were conducted in accordance with the procedures outlined in Picatinny Arsenal Technical Report 1401, except the determination of the heat of combustion of the experimental compounds, which was determined as follows:

A double valve self-sealing oxygen combustion Parr bomb was used, the water equivalent of which was 2779 cal/°C. One milliliter of water was placed in the bottom of the bomb before it closed. The bomb was flushed twice with oxygen at 10 atm pressure and filled with oxygen at 30 atm pressure. A single strand of fine iron wire was used for ignition and a correction of two calories per inch was allowed. The customary titration and correction was made for acidity.

RECOMMENDATIONS

It is recommended that further study be made of bis(2,2,2-trinitroethyl)urea in an attempt to produce a purer product, which may be less sensitive and more stable.

It is recommended that further study of methylenedinitramine (Medina) be undertaken in an attempt to stabilize it.

DISTRIBUTION LIST

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